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RECENT STUDIES OF CHEMICAL INTERACTIONS ON  
SURFACES USING MOLECULAR BEAMS

by

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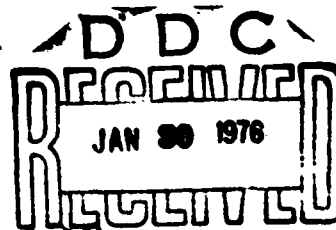
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Within the scope of this article will be included molecular beam studies of (i) chemisorption with special emphasis on "activated chemisorption," (ii) studies of heterogeneous chemical reactions including simple unimolecular decomposition, (iii) reactions with the surface or corrosion, and (iv) catalytic bimolecular reactions between distinct chemical species on the surface. A discussion of the experimental details of molecular beam techniques and their application to studies of chemical interactions on surfaces has been largely avoided since this topic has been thoroughly discussed in other recent articles.

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RECENT STUDIES OF CHEMICAL INTERACTIONS ON  
SURFACES USING MOLECULAR BEAMS \*

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I. INTRODUCTION

In 1970, Merrill reviewed the application of molecular beams to studies of gas-surface interactions related to catalysis.<sup>(1)</sup> Since that time there has been a rather impressive increase in the number of experimental studies in this area. More recently, Saltsburg has reviewed the dynamical aspects of gas-surface collisions, with some emphasis on beam experiments.<sup>(2)</sup> The latest advances in experimental techniques in molecular beam studies of reactive scattering and heterogeneous catalysis have been reviewed by Smith<sup>(3)</sup> and most recently by Madix.<sup>(4)</sup> The purpose of this review is to present both a comprehensive survey of the experimental work that has been reported subsequent to the review by Merrill and to focus critical attention on what is felt to be the more significant features of this work. While our first intent can be carried out rather objectively we have chosen to focus on those aspects of the work that relate more closely to our own research.

Within the scope of this article we will cover molecular beam work in the area of chemisorption, including a discussion of the phenomenon of

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"activated adsorption" and some of its implications, as well as studies of heterogeneous chemical reactions, including simple unimolecular decomposition, reactions with the surface itself and finally, surface catalyzed bimolecular reactions between distinct chemical species. A discussion of the experimental details of molecular beam techniques and their advantages for studies of chemical interactions on surfaces has been intentionally avoided, since several earlier articles have already covered these topics in some detail.<sup>(4-6)</sup>

It would be unfair to the reader and other workers in the field to suggest that the use of molecular beams, even when used in conjunction with modern surface analysis techniques, has resulted in a thorough and generally accepted understanding of even the simplest surface chemical processes. However, significant progress has been made in exploring the details of chemisorption and catalytic reaction mechanisms for a number of interesting chemical systems, and these advances are a hopeful indication of further progress to come.

## II. CHEMISORPTION KINETICS

Molecular beams have been used in a number of studies of adsorption on metal and semiconductor surfaces.<sup>(7-10)</sup> Kohrt and Gomer used an uncollimated effusive source to study CO adsorption on tungsten.<sup>(11)</sup> They found that the initial sticking coefficient of CO decreased with increasing gas or surface temperature. The angle of incidence of the beam was not varied in these experiments, however. Madey has also used uncollimated beams to deliver precise doses of gas to single crystal surfaces in ultra-high vacuum. Here, neither the temperature nor the angle of incidence of the beam was not varied in these studies. Other studies of adsorption have also been carried out using molecular beams, but in only a few cases have either the angle of incidence or the temperature of the beam been varied. This is unfortunate, since recent results indicate that these parameters may have a significant effect on the sticking coefficient, especially on smooth single crystal surfaces where the beam species experiences a single collision at a well defined scattering angle.

King and Wells have exploited the advantages of molecular beams to a greater degree by using well-collimated beams to study nitrogen adsorption on polycrystalline and single crystal faces of tungsten.<sup>(12)</sup> Their technique permits accurate measurements of the sticking coefficient,  $S$ , and the number of adsorbed atoms,  $N$ , by following the pressure increase in the target cell as a function of the time of exposure to the beam. They discuss several advantages of this technique over the flash-desorption method more commonly used to study adsorption kinetics. In addition to allowing a simplified experimental procedure, the use of sharply collimated molecular beams permits the adsorption study to be confined to a well-defined area of the surface, thereby minimizing the effects of crystal edges, supports, and vacuum walls. King and Wells varied the angle of incidence of the room temperature  $N_2$  beam on the surface but observed no angular dependence. However, the target in this case was a polycrystalline tungsten foil that was presumably rather rough on an atomic scale. Studies in which angular dependences of the sticking probability have been observed appear to be limited to cases where the preparation procedures have resulted in relatively smooth target surfaces, usually of single crystal material.

Evidently Hughes and Levinstein were the first to use interrupted or "modulated" beams to study adsorption kinetics on surfaces.<sup>(13)</sup> By using such a beam to slightly perturb the surface equilibrium coverage, a characteristic relaxation time  $\tau$  can be determined by simply measuring the exponential decay of the desorption flux or surface coverage with a suitable sensing instrument. This characteristic "sojourn" or lifetime on the surface usually varies with temperature in a manner given by

$$\tau = \tau_0 \exp(E_a/kT) ,$$

where  $E_a$  is the activation energy of the rate limiting step, e.g., the binding energy of the adatom to the surface, and  $\tau_0$  is a rather complex function of the degrees of freedom in the adsorbed state,<sup>(14)</sup> but usually ranges from  $10^{-12}$  to  $10^{-14}$  seconds. By measuring  $\tau$  as a function of the surface temperature,  $E_a$  and  $\tau_0$  can be determined. Arthur has used this technique to study the adsorption kinetics of various species including Ga,  $As_2$  and  $As_4$  on GaAs

crystal surfaces.<sup>(15-19)</sup> Surprisingly, they found that the characteristic temperatures of both scattered and desorbing  $\text{As}_2$  and  $\text{As}_4$  were well below the GaAs surface temperature, whereas for Ga on GaAs and  $\text{As}_2$  and  $\text{As}_4$  on Ga covered GaAs, the velocity distributions were characteristic of the surface temperature. Although the target was rotatable in their study, the angles of incidence and detection of the scattered and evaporated species were not reported. These data are of interest since it is expected that the deviations from the usual Knudsen law or cosine desorption flux. Arthur and Brown suggest that the evaporating  $\text{As}_2$  and  $\text{As}_4$  must carry the kinetic energy deficit in internal modes. However, their thermodynamic argument is not compelling in the absence of a detailed synthesis of the equilibrium condition.

Foxon, Boudry and Joyce have employed even more advanced techniques to study the kinetics of gas-surface interactions.<sup>(20)</sup> They have also reported adsorption-desorption kinetics for Ga and  $\text{As}_4$  on GaAs surfaces using signal averaging and fourier transform analysis of modulated beam data. This technique is, in principle, superior to phase sensitive detection in terms of the information obtainable from a single experiment. They did not observe desorption of  $\text{As}_2$  and  $\text{As}_4$  below the substrate temperature although their measurements were made in a regime where Arthur and Brown saw only slight deviations. Foxon et al. also report that the sticking of  $\text{As}_4$  on GaAs increases approximately two orders of magnitude when the surface temperature is raised from 600 to 900 K.

Temperature and angular flux anomalies have also been observed in molecular beam studies of adsorption and desorption for other gas-surface systems. Palmer et al. have used modulated molecular beams to study adsorption on epitaxially grown single crystal films of nickel and silver.<sup>(21)</sup> By carefully measuring the reflected flux as a function of the angle of incidence of the beam, relative sticking probabilities were obtained for hydrogen and helium on these surfaces. These measurements showed a distinct

angular dependence of the adsorption rate for  $D_2$  on Ni(111) and to a lesser extent on Ag(111) surfaces with the adsorption probability decreasing rapidly toward glancing incidence. Also, in this study, a beam of  $D_2$  was reacted with normal hydrogen (protium) chemisorbed on a Ni(111) surface and the angular distribution of the mixed species HD desorbing from the surface was measured. By modulating the beam and using a mass spectrometer to detect the HD in-phase signal by means of a lock-in type amplifier, only the signal resulting from the immediate reaction of the beam with surface hydrogen was obtained. Interestingly, the desorbing HD was found to have an angular dependence that was fit quite well by a function of the form  $\cos^d \theta$  where  $2.5 < d < 4.0$ , depending on the smoothness of the particular Ni(111) film being studied. Moreover, by conceptually synthesizing an equilibrium isotropic flux at the surface from a superposition of individual beams and invoking the "cosine law," the angular distribution for the desorption of hydrogen from Ni(111) could be obtained from the hydrogen reflection data alone. This internal consistency was not only satisfying experimentally, but demonstrated that basic thermodynamic principles such as microscopic reversibility and the cosine law could be used to relate the processes of adsorption, desorption and reflection. Palmer also found that the rate of chemisorption of hydrogen on 700 K Ni(111) depended on the beam temperature with an apparent activation energy of  $\sim 2$  kcal/mole which is consistent with their observed adsorption-desorption angular dependence. Krakowski and Olander have seen a similar energy dependence in a beam study of hydrogen dissociation on tantalum.<sup>(22)</sup> For a fixed target temperature, they measured a beam temperature dependence that indicated an activation energy of 1.4 kcal/mole for dissociation.

Smith and Palmer also studied  $H_2/D_2$  exchange on epitaxially grown Pt(111) films and obtained results similar to those on the nickel films.<sup>(23)</sup> Again, the sticking probability of hydrogen was found to decrease as the angle of the beam relative to the surface normal was increased and also increased with beam temperature, suggestive of an activation barrier to adsorption of about 2 kcal/mole. Smith and Palmer recently published the results of a study of the catalytic oxidation of a modulated molecular beam of  $D_2$ , also on Pt(111).<sup>(24)</sup> These results also reveal the same temperature

and angular dependences for the hydrogen chemisorption rates observed in the  $H_2/D_2$  exchange study.

Steinbruchel and Schmidt have also studied the angular dependences of the sticking coefficients of various gases such as  $H_2$ , CO,  $CO_2$ ,  $H_2$  and  $D_2$  on W(100) and W(110) surfaces using a simple molecular beam apparatus.<sup>(25)</sup> In general, they found that  $S(\theta_i)$  increases slightly toward grazing incidence. However, for  $H_2$  and  $D_2$  on W(110),  $S(\theta_i)$  decreases markedly toward grazing incidence in qualitative agreement with the results of Palmer and Smith on Ni(111) and Pt(111). Unfortunately, Steinbruchel and Schmidt could not vary the temperature of the beam to determine the energy dependences for chemisorption on W(110).

The experimental observation that in a number of cases  $S = S(\theta_i, T_B)$  is particularly interesting because these results challenge the traditional view of chemisorption. Langmuir proposed that chemisorption proceeds via a physisorbed or "precursor" state that allows a great deal of mobility along the surface. A physisorbed atom or molecule slides across the surface in this precursor state until a suitable "site" for chemisorption is encountered. We can imagine that in many cases a particular spatial orientation of the adsorbate at specific "sites" on the surface is required in order for chemical bonding to occur (steric effect) and that any activation barrier to this step must be overcome by energy input from the surface. This model leads us to expect that the probability for physisorption, and hence also chemisorption, is either constant or decreases as the temperature of the gas is increased. This is because trapping at the surface is only expected when  $kT_B < E_a$  where  $T_B$  is the beam temperature and  $E_a$  is the potential well depth of the precursor state.

Extensive molecular beam studies of both reactive and non-reactive scattering from smooth metal surfaces have demonstrated that, in most cases, the gas-surface interaction potential can be considered to be essentially one-dimensional in the direction of the local surface normal. In a few cases, such as on W(112),<sup>(26,27,35)</sup> there is significant periodicity in the plane of the surface giving rise to diffraction and "rainbow scattering."

However, one can usually consider that only the normal component of the velocity of an incoming particle is involved in the interaction with a metal surface. Since the effective gas temperature varies as the second power of the particle velocity, the surface sees a beam temperature that varies as  $\cos^2 \theta_1$ . From the above considerations it is expected that when  $kT_B \approx E_a$ , the sticking coefficient will increase as  $T_B$  is lowered or, equivalently, as the angle of incidence of the beam is increased. Of course, the experimental observation of the latter effect requires that the surface be smooth on an atomic scale so that random variations in the surface topography do not obscure the effect of changes in  $\theta_1$ . However, it is clear that the results for hydrogen indicate that for at least some surface conditions, a precursor state is not involved in the dissociative adsorption step since, in a number of cases,  $S$  has been found to increase as the velocity component normal to the surface is increased, either by raising the temperature of the beam or by decreasing the angle of incidence  $\theta_1$ .<sup>(21,25,28)</sup> Clearly then, we need to modify our picture of the chemisorption mechanism, at least for the case of hydrogen chemisorption.

Using basic thermodynamic considerations, it has been rigorously shown that gases which desorb with sharper-than-cosine distributions will also exhibit similar trends as hydrogen upon adsorption. Several papers have been written that develop the symmetry properties that that apply at the gas-surface interface including the relationship between adsorption and desorption.<sup>(29,30)</sup> One approach to understanding this relationship is to consider the necessity of the surface maintaining an equilibrium when the gas in question is in contact with it at the same temperature. In order to satisfy the second law of thermodynamics, the surface must return to the gas phase a distribution of particles that is both random in direction (isotropic) and Maxwellian in the speed distribution. Therefore, we can be sure that when a surface at the same temperature preferentially adsorbs gas-phase particles with certain velocities (speed and angle of incidence), the desorption flux will return to the

gas-phase a distribution of particles with just the exact angular and speed distribution to make up for the particles adsorbed. This is a statement of the so-called "cosine law," first expounded by Clausius.<sup>(31)</sup> This result was confirmed experimentally for the case of hydrogen on Ni(111) in the work of Palmer et al. mentioned above.<sup>(21)</sup>

Recent studies have shown that hydrogen is not the only species that exhibits this "anomalous" adsorption behavior. Recently, Palmer and Smith studied the oxidation of a CO beam on Pt(111).<sup>(32)</sup> Here, the product CO<sub>2</sub> was found to desorb with a distribution even more sharply peaked than for hydrogen and also of the form  $\cos^d \theta_r$ , where  $\theta_r$  is the scattered angle, and in this case  $d = 6$ . Using the cosine law relationship at the gas-surface interface, they predict that under the same surface conditions the chemisorption of CO<sub>2</sub>, presumably to give CO + O on the surface, will also decrease rapidly toward glancing incidence. Moreover, if a one-dimensional view of the gas-surface interaction is correct, then the sticking probability will increase markedly with beam temperature. This further implies that CO<sub>2</sub> desorbing from a platinum surface must also be somewhat "hotter" than the surface temperature in order to make up for the disproportionately greater number of higher energy-gas-phase molecules that are removed from the gas phase at equilibrium. Although no direct measurements of the energy distributions of CO<sub>2</sub> desorbing from Pt(111) have been made to verify this particular prediction, Kenney has measured the velocity distributions of hydrogen desorbing from both Ni(110) and polycrystalline nickel and found that the speed distribution was indeed characterized by a Maxwellian considerably in excess of the surface temperature (e.g., 1589 K compared to 1073 K).<sup>(33)</sup> Bernasek and Somorjai have also recently reported  $\cos^2 \theta$  desorption for CO<sub>2</sub> from stepped Pt(111) surfaces.<sup>(34)</sup>

Cardillo and coworkers have recently published the results of a careful study of hydrogen adsorption on the (100), (110), and stepped (100) crystal faces of copper.<sup>(28)</sup> In this work they used a supersonic "nozzle" source that yields a very narrow range of velocities in the beam. They studied the dissociative adsorption probability as a function of beam energy and

angle of incidence. By reacting the  $H_2$  beam with adsorbed D atoms, as in the earlier work of Palmer et al. on Ni and Pt(111),<sup>(21,23)</sup> the desorption distribution of the mixed species HD was measured. Isotopic "labeling" in these studies is a convenient technique for identifying only those hydrogen molecules that recombine and desorb from the surface. It has been shown that isotopic effects in the desorption angular distribution are negligible.<sup>(28)</sup> This assumption is also supported by the equilibrium synthesis data of Palmer in which the adsorption of  $D_2$  is compared with the desorption of HD.<sup>(21)</sup>

The conclusions reached by Cardillo et al. from their data on copper surfaces were that: (i) there is a significant energy barrier to the dissociative adsorption (chemisorption) of hydrogen and that it acts perpendicular to the surface normal; (ii) the barrier height or activation energy for this chemisorption depends significantly on the particular crystal face exposed; and (iii) that the presence of steps and ledges on Cu(100) did not significantly affect either the adsorption or desorption behavior of hydrogen.

Although the work of Cardillo et al. does not rule out the possibility of a parallel chemisorption path involving a precursor state, under the conditions of their experiments, hydrogen can bypass any such physisorbed configuration and chemisorb directly when the necessary activation energy is supplied in the form of kinetic energy to the incident molecule. While the results of Cardillo et al. militate against a precursor state in the chemisorption path of hydrogen on copper, they do indicate the existence of preferred surface sites for chemisorption. Moreover, by comparing the limiting adsorption probabilities on the two crystal faces studied, a reasonable guess can be made as to the locations of these sites in the surface lattice.

Stoll has used beams to study the chemisorption of oxygen on smooth single-crystal Pt(111).<sup>(35)</sup> He compared the steady-state oxygen surface coverages with 20 and 330°C oxygen beams at surface temperatures of 250 and 350°C. The equilibrium surface coverage with a hot beam was nearly twice that for a cold beam on the 350°C surface, indicating a proportionately greater sticking coefficient for the hot oxygen. These results suggest an activation energy for oxygen chemisorption of about 1 kcal/mole. However,

for a surface temperature of 250°C, Stoll reports that the steady-state coverages are more nearly the same for both hot and cold beams. In this temperature regime, a clean-off reaction with residual CO is probably the dominant mechanism for the removal of surface oxygen and the surface oxygen coverage should scale directly as the adsorption rate. Stoll offers no explanation for the different adsorption characteristics at the two surface temperatures. However, Merrill has also observed that hydrogen chemisorption on Pt(111) is unactivated below 300°C<sup>(36)</sup> whereas Smith and Palmer's results indicate an activation energy of about 2 kcal/mole on 650°C Pt(111).<sup>(23)</sup> These results suggest the possibility that the chemisorption transition probability is rather sensitive to the surface temperature. This may involve the entropy change in going to the mobile chemisorbed state. Procop and Volter report an entropy increase of about 20 cal/mole °K for hydrogen chemisorption on platinum, for example.<sup>(37)</sup> Stoll's results were over relatively narrow temperature ranges (beam and surface) and no measurements of adsorption rates as a function of angle of incidence were obtained so that further work in this area would be helpful.

Recent molecular beam studies have made some important contributions to our understanding of adsorption-desorption phenomena. However, two important questions have been raised. First, under what conditions does one expect to find activated chemisorption of gases such as hydrogen and oxygen on metal surfaces, e.g., does it apply only to dissociative adsorption or can we expect similar results for other species on a wide range of surfaces? Second, what factor or factors are responsible for the widely varying results that are still being reported for the sticking probabilities of gases by various workers using nominally identical, clean, single crystal surfaces? Recently reported values for the sticking coefficient of oxygen on Pt(111), for example, range from  $S = 10^{-6}$  to  $S = 0.2$ .<sup>(38,39)</sup>

Regarding this second question, a detailed examination of the various possible factors involved in each case would not be appropriate here. However, a few general remarks regarding the essential ingredients of a

reproducible gas-surface interaction study can be made. First, it is extremely important to specify both the angle of incidence and temperature (energy) of the gas being studied. Further characterization of the beam as to energy (e.g., monoenergetic) and various internally excited states can also be considered. The surface, of course, must be well-characterized. This means, in practice, clean, smooth, single crystal surfaces. Many of the recent studies of gas-surface interactions have specified the surface cleanliness, via AES (Auger electron spectroscopy) for instance, and the crystal structure by LEED (low energy electron diffraction). However, in general, one expects that rough surfaces provide a large number of unspecified sites that may significantly affect the sticking probability or change the effective area of the surface through multiple collisions, and considerable care must be taken to avoid this condition. Presently, the most sensitive technique for characterizing the smoothness of clean surfaces on an atomic scale is by the scattering of noble gas atoms, especially helium. The smoothness of similar crystal surfaces used in various laboratories are more readily evaluated when the scattering distributions, or at least the peak height and FWHM data for a well collimated room temperature helium beam are available for comparison. Without further refinement, however, this technique is not suitable for comparisons of surfaces with less than one percent of the total area "rough" on an atomic scale, and this still represents a very large defect density on the surface.

Perhaps the most difficult problem in surface characterization is achieving a clean or contaminant free surface. Diffusion from the bulk and adsorption from the gas phase of various unwanted species is a constant problem, even in ultra-high vacuum. Surface chemical analysis techniques such as AES, INS (ion neutralization spectroscopy), SIMS (secondary ion mass spectrometry), UPS (ultraviolet photoelectron spectroscopy), and XPS (X-ray photoelectron spectroscopy) or ESCA (electron spectroscopy for chemical analysis), used separately or in conjunction, are some of the ways that the chemical composition and even the oxidation states at the surface can be determined.

In studies on clean surfaces, possible "clean-off" reactions involving ambient species such as CO, H<sub>2</sub> and O<sub>2</sub> should be considered. For example, Joebstl has studied the effects of small amounts of CO on the adsorption of O<sub>2</sub> on Pt(111) in ultra-high vacuum.<sup>(40)</sup> Oxygen can be removed from platinum by reaction with adsorbed CO to form CO<sub>2</sub>. Since the sticking probability for CO is greater than for O<sub>2</sub> on platinum, especially on the low index faces [e.g., S(CO)/S(O<sub>2</sub>) ≈ 10<sup>2</sup> on Pt(111)],<sup>(32)</sup> relatively small amounts of CO can be very important. It appears likely from Joebstl's work that many studies of O<sub>2</sub> adsorption on platinum have probably been seriously affected by small amounts of CO produced by hot carbon covered surfaces such as ion gauge filaments, etc.

Finally, we can expect that, in general, the sticking coefficient will also depend on the surface temperature so that the temperature of the surface under study should be varied over a reasonably wide range in order to determine this dependence explicitly. A surface temperature dependence may arise for a variety of reasons including the likely entropy difference between the gaseous and adsorbed states involved in the adsorption. Statistical-mechanical or "transition-state" theories predict, in general, that the transition probability  $k$  will be of the form

$$k = P T^r \exp\left(\frac{\Delta S}{R} - \frac{Q}{RT}\right) \quad (P, r, Q \text{ independent of } T)$$

with small positive or negative values assigned to  $r$ , depending on the details of the theory.<sup>(41)</sup>

With regard to the question of activated chemisorption, we have already pointed out that desorption studies indicate that the dissociative adsorption of CO<sub>2</sub> is also highly activated on Pt(111). In fact, from the analysis of Cardillo et al.<sup>(28)</sup> and the shape of the desorption distribution, we expect  $E_a \sim 6$  kcal/mole for CO<sub>2</sub> on 475 to 875 K platinum. Also, Stoll's work indicates that oxygen adsorption on Pt(111) is slightly activated above 250°C.<sup>(35)</sup>

In addition to the activation of chemisorption via kinetic energy, recent studies suggest that vibrational excitation is also a mode of activation for certain chemical reactions.<sup>(42,43)</sup> For example, Steward and Ehrlich report that vibrational excitation facilitates the chemisorption of methane on a

rhodium substrate.<sup>(42)</sup> They also point out that the usual transition-state theory of chemical rates fails to account for the large kinetic isotope effects they observed in the chemisorption of normal versus deuterated methane. These results suggest that detailed studies of the energetics of chemisorption processes are likely to have a profound impact on our understanding of chemical rates in general.

### III. HETEROGENEOUS REACTION STUDIES

#### A. Unimolecular Reactions

There have been several recent studies of unimolecular reactions on surfaces using molecular beams. Dahlberg, Fisk and Rye have studied the much investigated decomposition of formic acid on polycrystalline platinum foil.<sup>(44)</sup> A beam of formic acid was directed onto a fixed platinum target and the scattered formic acid and decomposition products detected by line-of-sight mass spectrometry. The detected products of the decomposition were CO, CO<sub>2</sub> and H<sub>2</sub>. H<sub>2</sub>O could not be detected because of the noise contributed by a large ambient background level of this species. The CO<sub>2</sub> and H<sub>2</sub> rates of production were equal, as expected from the one-step decomposition of HCOOH. CO was produced at about one-tenth the CO<sub>2</sub> rate at 900 K and the CO/CO<sub>2</sub> ratio increased with temperature. These results were complicated by a surface contaminant that could be removed by heating the platinum above 1150 K. Surface contamination is not surprising considering their base vacuum of only  $3 \times 10^{-7}$  torr. Although the contaminant was not identified, the temperature dependence suggests oxygen or a clean-off reaction involving oxygen. Neither the contamination rate below 1150 K nor the clean-off rate above this temperature was affected by exposure to HCOOH and, therefore, HCOOH was ruled out both as the source of the contaminant, and the source of oxygen in a clean-off reaction. They also observed that the rate of decrease in the decomposition rate from the presumably clean surface conditions to the steady-state contaminated surface increased rapidly as the surface was cooled, while the initial activity also increased with decreasing temperature, at least down to 600 K.

Fenn and his coworkers at Yale have utilized a nozzle beam source in a novel closed-loop catalytic reactor system in which the beam is scattered from a catalytic target and then recycled through the nozzle source, using a mercury diffusion and mechanical bellows pumps in series.<sup>(44)</sup> The technique allows the reaction rate to be enhanced by the number of passes of the reactant gas through the system, but requires that reactions on the various system surfaces and in the gas phase not be overwhelming compared with the rates on the target. Using this method, Fenn has studied the isomerization of cyclopropane to propylene on a molybdenum oxide surface. Surprisingly, the reaction rate was independent of the molybdenum oxide temperature (from 400 to 700°C) but varied strongly with the beam energy with an activation energy of about 20 kcal/mole. Fenn suggests that the cyclopropane must be vibrationally excited in order for isomerization to occur. This work demonstrates the importance of catalytic studies where the internal and kinetic energies of the reacting species are controlled. Also, since nozzle sources are capable of generating substantial mass fluxes, it is not unreasonable to consider the use of such a system for chemical processing in commercial quantities in order to increase the efficiency and/or selectivity of a reaction. An important new field of "non-equilibrium catalysis" is suggested by this work and further investigations of the type undertaken by Fenn and others using nozzle beams should be actively pursued.

The decomposition of  $N_2O$  has been studied by West and Somorjai on clean and carbon-covered Pt(100)<sup>(45)</sup> and by Mischlitz and coworkers on polycrystalline tungsten surfaces.<sup>(46)</sup> While Mischlitz's results indicated that adsorption of the  $N_2O$  molecule was required for dissociation, Somorjai's results on carbon-covered Pt(100) suggest that dissociation can occur without full accommodation with the surface as is indicated by the directed nature of the NO signal. Diffuse emission of NO from a carbon free Pt(110) surface was observed by Somorjai, however. Mischlitz's work suffers from a lack of adequate surface characterization and although the scattering of  $N_2$  and NO was somewhat directed, surface roughness was probably a significant

factor. This roughness coupled with the scatter in the data and the limited range of angles measured makes their conclusion regarding diffuse scattering and full accommodation of the  $\text{H}_2\text{O}$  beam and its products suspect. Somorjai's results are also somewhat speculative. A problem inherent in both of these studies is the ambiguity of the mass-spectrometer signals for both  $m/e = 28$  ( $\text{N}_2$  or  $\text{CO}$ ),  $m/e = 44$  ( $\text{N}_2\text{O}$  or  $\text{CO}_2$ ) and the problem of dissociative ionization of the scattered  $\text{N}_2\text{O}$  to produce both  $\text{N}_2^+$  and  $\text{NO}^+$ . For this reason, any conclusions regarding these investigations should probably be considered tentative.

Schutte, Scoles and Tommasini have reported an investigation of the recombination of atomic hydrogen on condensed surfaces of  $\text{H}_2\text{O}$ , He and Ar in the range 2-15 K.<sup>(47)</sup> Apparently, most of the energy of recombination (4.5 eV) is carried away by the desorbing  $\text{H}_2$  molecule, but a monolayer coverage of  $\text{H}_2$  increases the energy transfer by an order of magnitude. Melin and Madix have also studied the energy transfer to the surface from hydrogen atom recombination on polycrystalline Ni, Cu, Pt and Ag wires in a flowing rf discharge and found the energy transferred to the first three materials to be markedly less than on Ag.<sup>(48)</sup> Molecular beam studies support these results inasmuch as the angular desorption distributions measured in molecular beam studies of hydrogen atom recombination on single crystal surfaces of Ni, Cu, and Pt indicate that the desorbing hydrogen molecules are indeed "hotter" than the surface temperature, and a study of the angular sticking dependence of  $\text{D}_2$  on Ag(111) indicates a similar trend although less pronounced than on Ni, Cu, or Pt.<sup>(21)</sup> More nearly diffuse and isothermal desorption of hydrogen and a much smaller activation barrier would thus be expected on Ag, in qualitative agreement with Madix's results.

#### B. Reactions with Surfaces

Molecular beams have been used more frequently in studies of heterogeneous reactions where the beam species reacts directly with the surface. Olander and coworkers have used modulated beams of molecular oxygen to study the oxidation of graphite on both the basal and prism planes.<sup>(49,50)</sup>

The kinetics of this reaction evidently involves a competition between the generation of active sites for the initial oxidation step through the removal of carbon atoms from the surface, and deactivation of the surface by annealing. Recently Shih, Liu and Baron have also studied the oxidation of graphite by molecular and atomic oxygen beams.<sup>(51-53)</sup> Olander's results were for fixed angles of incidence and reflection ( $\theta_i = \theta_r = 45^\circ$ ), whereas Shih et al. varied both angles in their work. They measured diffuse (cosine) scattering of molecular oxygen from their target indicating a rather rough surface and/or fairly complete accommodation of the oxygen. However, the CO desorption flux was proportional to  $\cos^2 \theta$  so that their surface was not so rough as to totally obscure angular effects in the scattering. These beam studies of graphite oxidation indicate the following additional points: (i) the principal reaction product is CO whereas CO<sub>2</sub> is produced at a rate at least two orders of magnitude less than the CO rate; (ii) there is little or no beam temperature dependence of the reaction rate and the graphite surface temperature effects primarily the oxidation by O<sub>2</sub>; (iii) the reaction with O atoms is about one order of magnitude more probable than for O<sub>2</sub>; and (iv) the reaction rates for both O and O<sub>2</sub> beams exhibit maxima at a surface temperature of about 1300 K indicating a competition between surface atom mobility and the annealing rate of active surface sites.

Madix and coworkers have also studied the reactions of silicon and germanium surfaces with modulated beams of O, O<sub>3</sub>, and Cl<sub>2</sub>.<sup>(54-59)</sup> As in the work of Olander,<sup>(5,49,50)</sup> Madix utilizes the information contained in the phase relationship of the product signal to derive the kinetics of the reaction. He refers to this technique as "molecular beam relaxation spectroscopy" (MBRS). A detailed discussion of the analysis of modulated signals in studies of reaction kinetics has been given by Olander<sup>(5)</sup> and more recently by Schwarz and Madix.<sup>(6)</sup>

Lintz, Pentenero and their coworkers in France have used beams of noble gases in a different approach to studies of chemical reactions with surfaces. They have utilized noble atom surface scattering to study the

kinetics of the oxidation of various metal surfaces.<sup>(60-64)</sup> Their method relies on the markedly different scattering properties of a clean and adsorbate covered surface. If the surface is clean and relatively smooth, sharply directed scattering near the specular angle will result, whereas the scattering from various adsorbates on the surface will generally be diffuse. Thus, by monitoring the directed scattering intensity, the surface coverage can be followed during the course of the reaction. Using this technique, Lintz, Pentenero et al. have determined important binding states and heats of desorption involved in the kinetics of surface oxidation by measuring surface coverages as a function of metal temperature and gas pressure. The technique suffers from the problem that, in many cases, the morphology of the surface may change during the course of the reaction and thereby alter the specularity of the clean surface. This technique has also been used by Palmer and Smith to study the kinetics of CO oxidation on a smooth platinum catalyst that was not consumed in the reaction.<sup>(32)</sup>

### C. Bimolecular Reactions

Surface catalyzed bimolecular reactions are perhaps the most experimentally difficult type of surface chemical process to study using molecular beams. This fact may be partially responsible for the relative lack of activity in this area. However, a few bimolecular reactions have now been reported and this work will undoubtedly stimulate further heterogeneous reaction studies using beams in the near future.

The first reported study of a surface catalyzed bimolecular reaction using beams was by Smith and Palmer.<sup>(24)</sup> They studied the oxidation of deuterium on epitaxially grown Pt(111) films. In this work the platinum target was exposed to an ambient of  $^{16}\text{O}_2$  ( $10^{-6}$  to  $10^{-5}$  torr). A modulated (100 Hz) beam of deuterium was directed at the oxygen covered target and the scattered beam and reaction product ( $\text{D}_2\text{O}$ ) was detected using a mass spectrometer and phase sensitive (lock-in) amplifier. At elevated temperatures the target was presumably kept clean of typical vacuum species such as carbon monoxide, hydrogen, hydrocarbons, and surface carbon by clean-off reactions with the oxygen ambient. In support of this conclusion, it was

found that intense specular helium reflection from the surface could be maintained in the presence of a small ( $\sim 10^{-7}$  torr) oxygen ambient where evidently the rate of contamination was just compensated for by the rate of clean-off via oxidation. The activated adsorption of the  $D_2$  beam on this "clean" Pt(111) surface was investigated and has already been discussed. Generally, a heated  $D_2$  beam was used in the reaction with surface oxygen in order to obtain the maximum adsorption rate and thereby increase the product signal.

The reaction was found to be nearly first order in  $O_2$  pressure whereas the  $D_2$  beam flux dependence exhibited three regimes,  $p^{1/2}(D_2)$ ,  $p(D_2)$ , and  $p^2(D_2)$ . The second order dependence suggested an improbable mechanism involving four hydrogen atoms. However, the reaction mechanism probably involves only two surface hydrogen atoms and a surface oxygen atom and the second order dependence may be an artifact of the beam method as will be discussed below.

The phase lag of the  $D_2O$  product signal as a function of temperature indicates an activation energy of about 12 kcal/mole for the rate limiting step. However, the interpretation of these data depends on the order of the reaction as has been pointed out by Madix,<sup>(6)</sup> and a somewhat lower value for the activation energy of the reaction is probable. Hydrogen atom diffusion may be rate limiting if an activation energy less than 10 kcal/mole is assumed. The angular distribution of the desorbing  $D_2O$  was approximately cosine, so the adsorption of water on Pt(111) at 925 K is apparently not activated.

Smith, Palmer and Vroom also attempted to study the catalytic oxidation of  $C_2H_4$  on Ag(111) epitaxial films by molecular beams.<sup>(65)</sup> However, no oxidation products could be detected with a  $C_2H_4$  beam impinging on a Ag(111) target exposed to oxygen. With an isotropic pressure of both gases at higher pressures, the reaction product  $CO_2$  could just be discerned, however. Dissociation of the  $C_2H_4$  beam over Ag(111) at 575 K to form  $C_2H_3$  (10%) and  $C_2H_2$  (5%) was also inferred from a comparison of the relative intensities of these ion peaks in the direct versus the scattered beam.

Palmer and Smith have also reported a molecular beam study of the oxidation of CO, again on Pt(111).<sup>(32)</sup> As was mentioned earlier, they found that the angular desorption distribution of the CO<sub>2</sub> product in the surface temperature range from 475 to 875 K was characterized by  $\cos^6 \theta$ , indicating that CO<sub>2</sub> adsorption at these temperatures is activated on Pt(111). Weinberg and Merrill have also predicted a large activation energy for CO<sub>2</sub> adsorption on platinum using their CFSO-BEBO model of adsorption.<sup>(66)</sup> The oxidation reaction appears to proceed mainly via a Langmuir mechanism with CO diffusing rapidly across the surface above 450 K. Chemisorbed CO apparently blocks the chemisorption of oxygen in the central region of the beam spot and thus poisons the reaction in the temperature-pressure regime where the surface coverage of CO is high. The high surface mobility of CO coupled with this poisoning effect combines to produce an interesting boundary effect at the perimeter of the beam spot on the surface. The high surface mobility of CO results in a rapid reaction rate at the perimeter of the beam spot on the platinum surface, giving an anomalous rise in the reaction rate at high beam fluxes. It is possible that a similar contribution resulting from deuterium diffusion is also responsible for the appearance of a second order D<sub>2</sub> pressure dependence at high beam fluxes in the earlier study of D<sub>2</sub> oxidation. Gomer has also suggested that molecular hydrogen diffuses very rapidly across hydrogen covered areas of platinum, followed by dissociative adsorption on the clean surface.<sup>(67)</sup>

In the CO oxidation study, Palmer and Smith fit their observed data using the Langmuir kinetic equations, but this required that the principal mechanism for removal of surface oxygen be by direct desorption as atoms. This latter assumption is not likely at the temperature of their work. However, other evidence strongly indicates that a Langmuir rather than a Rideal mechanism is operating. On the other hand, their data can also be fit quite nicely using the Rideal kinetic equations and does not require the assumption of direct desorption of oxygen atoms. However, this does not mean that both the chemisorption and migration of CO are not involved in

the reaction path. Rather, the tacit assumption in the Langmuir formula is that the probability of reaction does not depend on the point of impact of the reactant gas on the surface but only on its average coverage  $\theta$ . At equilibrium, the kinetic balance of the reaction in this case has the familiar form

$$\rho_A(1-\theta_A-\theta_B) = k \theta_A \theta_B$$

(adsorption rate) = (reaction rate) ,

where  $\rho_A$  is the impact rate and  $\theta_A$  is the surface coverage of reactant A, and  $\theta_B$  the coverage of reactant B. Alternatively, a Rideal formulation is based on the idea that a gas phase reactant must impact directly on, or adjacent to a second chemisorbed reactant, e.g., within the covered area  $\theta_A$ . Then we have

$$\rho_A(1-\theta_A-\theta_B) = k \rho_B \theta_A$$

where  $\rho_B$  is the impact rate of species B that presumably reacts by direct impact, or near miss, on reactant A. However, it seems likely in cases where a competing channel for species B exists (e.g., via desorption) that the probability of reaction falls off rapidly as the point of impact of B increases in distance away from reactant A. This can be true even though both the chemisorption and migration of species B is involved in the reaction path, as is assumed in the Langmuir model. For this case we can write the kinetic equation as

$$\rho_A(1-\theta_A-\theta_B) = k \rho_B \theta'_A$$

where  $\theta'_A$  now represents some effective area surrounding each chemisorbed molecule A. Such a "quasi-Rideal" mechanism may be important in the oxidation of CO on Pt, for example. Unfortunately, this possibility leads to some confusion since we can no longer distinguish the mechanism solely on the basis of the kinetics of the reaction. It appears important, therefore, to clearly distinguish between reactions that obey Rideal kinetics and reactions where it is believed from more detailed evidence that a true Rideal mechanism is operating.

Recently, Palmer has completed a similar study of the catalytic oxidation of the  $C_2$  hydrocarbons, also on Pt(111).<sup>(68)</sup> Here, the results are somewhat more involved, including the fact that three reaction products are observed, CO,  $CO_2$  and  $H_2O$ . The reactions proceed via a surface acetylenic species that results from the adsorption of the  $C_2$  hydrocarbons at elevated temperatures on platinum. The chemisorption of  $C_2H_6$  is somewhat activated with a sticking coefficient of less than 0.05 whereas the chemisorption of  $C_2H_4$  and  $C_2H_2$  are not. The sticking coefficient for  $C_2H_2$  is near unity on Pt(111) while for  $C_2H_4$ ,  $S \sim 0.5$ .

The angular desorption distributions of the reaction products of CO and  $CO_2$  were measured and neither were simple cosine. In the case of  $CO_2$ , the distribution appears to be composed of a higher order cosine ( $\cos^6 \theta$ ) superimposed on a broader-than-cosine desorption pattern. From the two-component nature of the desorption of  $CO_2$  (and possibly CO) it appears that there are two distinct channels for the formation of this species. Since in a previous study, the formation of  $CO_2$  from CO adsorbed on the surface resulted in only simple higher order cosine desorption, it is tempting to ascribe the difference in the present case to a local perturbation of the interaction potential or a distinct binding site induced by the presence of another chemisorbed species such as carbon on the surface. This is the first reported observation of broader-than-cosine desorption and indicates that the molecular species can desorb directly from a potential below that of the gas, i.e., with a negative activation energy. From this model we also expect the "temperature" of the desorbing molecules to be less than the surface temperature, in analogy with the effects of a positive activation energy.

Measurements of the rates of evolution of CO,  $CO_2$  and  $H_2O$  from the oxidation of the  $C_2$  hydrocarbons as a function of the platinum surface temperature indicate a common rate-limiting step for all three species

with an activation energy of 16 kcal/mole. The energy of this barrier is about the right value for the surface diffusion of atomic oxygen. Thus, the oxidation reaction apparently proceeds via a Langmuir mechanism with oxygen migration rate limiting at high oxygen pressures and low to intermediate temperatures. By using a mixture of normal and deuterated acetylene in the beam it was determined that the reaction to form water occurs in two steps, presumably via an OH intermediate. Also, the reaction kinetics indicate that the formation of  $\text{CO}_2$  also occurs in two steps by the further oxidation of surface CO.

Bernasek and Somorjai have recently used molecular beams to study  $\text{H}_2/\text{D}_2$  exchange on platinum single crystal surfaces.<sup>(69)</sup> They studied this reaction on a nominally step-free Pt(111) surface and on Pt(997) and Pt(553) surfaces consisting of steps separated by (111) oriented terraces nine and five atoms wide, respectively. Earlier work by Somorjai and coworkers have demonstrated the importance of steps in the catalytic behavior of platinum surfaces.<sup>(70-72)</sup> In the present investigation the stepped surfaces were considerably more active than the nominal Pt(111) surface at pressures below  $10^{-6}$  torr. Their data suggest, however, that at higher hydrogen pressures the Pt(111) surface becomes relatively more active and that the differences also depend on the beam modulation frequency. In this regard, they compare their work to that of Lu and Rye, using the flash desorption method, in which no dependence on step density was observed.<sup>(73)</sup> Apparently, the surface diffusion of hydrogen to active sites occurs rather slowly compared with the beam modulation period, even at 40 Hz.

Both amplitude and phase data as functions of the modulation frequency were obtained in this beam study and evaluated to determine the rate parameters of the reaction. Below about 600 K Bernasek and Somorjai report that the rate of HD formation is described by a pre-exponential of  $8 \pm 1 \times 10^5 \text{ sec}^{-1}$  and an activation energy of  $4.5 \pm 0.5 \text{ kcal/mole}$  with a sharp transition at higher temperatures to a pre-exponential of  $1 \pm 2 \times 10^2 \text{ sec}^{-1}$  and an activation energy of  $0.6 \pm 0.3 \text{ kcal/mole}$ . These activation energies are a good fit to the slopes in an Arrhenius plot of the amplitude data in

these respective regions. However, Bernasek and Somorjai's pre-exponential constants specify a transition temperature in the region of 260 K, in disagreement with their data, so there appears to be some error in the calculation of these parameters in this work.

The HD exchange data were obtained by introducing  $D_2$  via a high pressure multichannel beam source and the  $H_2$  isotropically above the surface.  $H_2/D_2$  mixed beams and a hydrogen beam with a deuterium ambient was also investigated. Bernasek and Somorjai report that their results were independent of the method of reactant introduction. However, this statement is not borne out by a comparison of the HD exchange rate as a function of the beam and ambient pressures where significant differences are apparent. Nevertheless, on the basis of these results, together with the temperature dependence data, Bernasek and Somorjai suggest a two branch mechanism, with a Langmuir-Hinshelwood process dominant below 600 K and a Rideal-Eley mechanism dominant at higher temperatures. However, it appears possible that a more simplified explanation would also be consistent with most of their published results. Assuming that the reaction is indeed independent of the method of introduction of the reactants and that random mixing of the dissociatively adsorbed hydrogen occurs on the surface, then the probability of formation of HD on the surface will be proportional to  $\frac{2[H][D]}{[H] + [D]}$  with the probability for formation of  $H_2$  and  $D_2$  given by  $\frac{[H]^2}{[H] + [D]}$  and  $\frac{[D]^2}{[H] + [D]}$ , respectively. A plot of the probability of HD formation versus either of the reactant concentrations ( $[H]$  or  $[D]$ ) gives a good fit to both the beam and ambient pressure dependences reported by Bernasek and Somorjai, provided the equivalent beam flux at the surface is reduced by about half an order of magnitude, relative to the  $H_2$  background. Bernasek and Somorjai did not measure the beam flux directly, but rely on a previous study of the characteristics of a similar source. This uncertainty may be coupled with possible sources of error in the measurement of the  $H_2$  ambient to give the total relative error suggested by the random mixing model. In lieu of such an error in the beam flux relative to the ambient hydrogen pressure, the differences in the pressure behavior of the beam and the

ambient must be attributed to an artifact resulting from chopping of the deuterium beam, resulting in a very different interpretation of the kinetic data.

Bernasek and Somorjai have also obtained reaction probabilities for beams of  $O_2$ ,  $N_2$  and CO reacting in various combinations with  $H_2$ ,  $O_2$  and CO over stepped platinum surfaces.<sup>(74)</sup> Also investigated were the decomposition of HCOOH and  $CH_3-NH_2$  to yield  $CO_2$  and  $NH_3$ , respectively. These results demonstrate that there are a number of catalytic reactions which are amenable to study by molecular beam methods.

#### IV. CONCLUSION

Perhaps the single most important recent development in the field of surface chemistry and catalysis has been the increasingly multidisciplinary approach to the understanding of these phenomena. This trend has been promoted by the development of a number of new experimental techniques for examining, in detail, the physical and chemical properties of the surface. Electron and ion scattering, various electron and photon spectroscopies and numerous other experimental techniques including the use of molecular beams are being used increasingly in studies of chemical interactions on surfaces. The widely varying backgrounds and viewpoints represented by these specialized disciplines require a high degree of cooperation among these investigators in order to more readily codify the various experimental results that are being reported and to permit a more complete understanding of the underlying principles.

Molecular beams have played an important role in studies of reactive interactions in the gas phase and their application to studies of chemical interactions on surfaces will undoubtedly be of similar importance. The objective of these studies is to permit a detailed description of the action of the surface in catalyzing various chemical reactions. It is often stated that the action of a catalyst is to reduce the activation energy barrier to the reaction. However, of considerable importance are geometrical or steric considerations and the entropies of the various

states involved in the reaction path. The importance of these additional factors has been clearly demonstrated by numerous cases where electronically similar surfaces exhibit dramatically different catalytic properties.

Historically, conflicting experimental results have been typical in studies of catalysis and much of the blame for these discrepancies has been laid to the uncertain physical and chemical nature of the catalytic surfaces that were studied. However, a number of researchers are now using modern experimental techniques to achieve what are believed to be well-characterized, reproducible surfaces. It is, therefore, appropriate that when results on nominally identical single crystal surfaces appear to be in conflict, a careful examination be made for other less obvious factors that may be important. For example, the chemisorption of hydrogen and oxygen has been reported to be unactivated at low surface temperatures on clean platinum surfaces.<sup>(36,75,76)</sup> However, beam studies at higher surface temperatures have indicated an activation barrier to the chemisorption of these species.<sup>(23,24,35)</sup> One study has indicated that surface contamination is responsible for the activated adsorption of hydrogen on nickel.<sup>(77)</sup> However, there is also considerable evidence to the contrary.<sup>(21,33)</sup> Alternatively, we have pointed out that the surface temperature is apparently an important parameter in the chemisorption of hydrogen and oxygen on platinum and methane on tungsten. The surface temperature is probably a factor in other gas-surface adsorption systems as well, especially in dissociative adsorption involving an increased entropy of the chemisorbed state. Undoubtedly, the further investigation of this and other questions related to catalysis will provide molecular beam researchers with important areas of study for some time to come.

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